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14. ABSTRACT

These briefing charts are an overview of reduced toxicity, high performance monopropellant. Performance of hydrazine limits spacecraft payload, range, lifetime and operational response time. The focus is to replace SOTA Hydrazine with monopropellants based on energy dense ionic liquids.

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THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER

REDUCED TOXICITY, HIGH PERFORMANCE MONOPROPELLANT

September 2011

Mr. Adam Brand
AFRL/RZSP
US Air Force Research Laboratory

Current Propellant Safety Issues & Performance Drivers

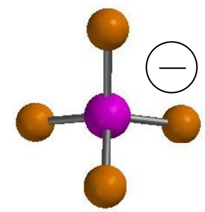
- **Hydrazine vapor toxicity can increase testing/operations costs:**
  - **System Handling/Fueling by certified crews in high level PPE**
  - **Monitoring system in field**
- **Vapor toxicity can limit transportation options**
- **Performance of hydrazine limits spacecraft payload, range, lifetime and operational response time**

System Handling/Fueling

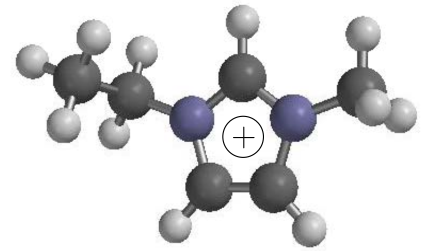
Desire improved volumetric impulse for greater capabilities and elimination of vapor toxicity with acceptable safety properties

Energetic Ionic Liquids-
Avenue to Hydrazine Replacement

- **History**
  - An ionic compound that has a melting point at or below 100ºC
  - Seminal work at USAFA (Wilkes et.al.)
  - Industrial solvents, green chemistry
    - Low vapor pressure, low vapor toxicity
    - Wide solubility ranges

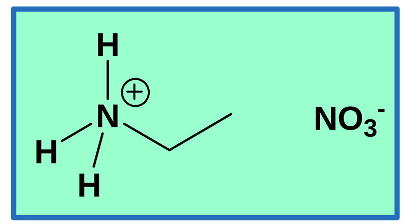


$AlCl_4^-$



EMIM cation
(1-ethyl-3-methylimidazolium)

- **ILs as *Energetic* Materials**
  - First energetic ILs: chemical oddities
  - AFRL realizes chemical structure manipulation leads to new classes of highly, energy dense materials (HEDM) for advanced propulsion



Liquid propellants:
Spacecraft thrusters
Booster engines
DACS/ACS

Energetic ionic liquids employed to produce advanced monopropellant, AF-M315E

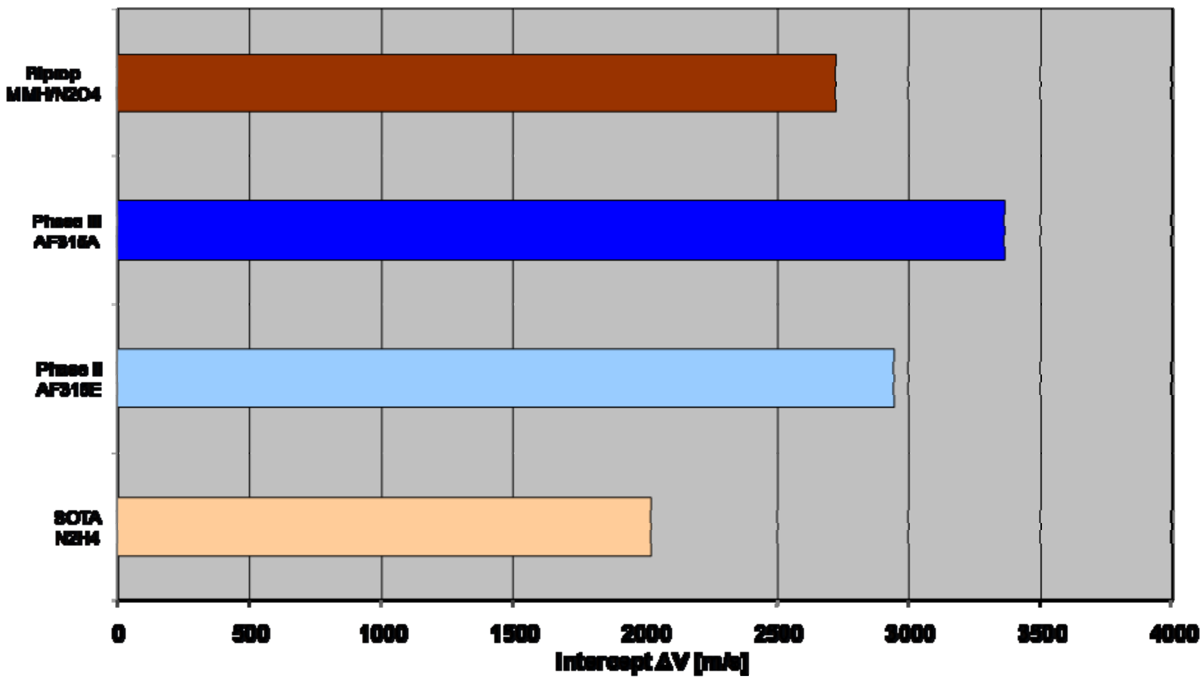
AF-M315E Desirable Properties

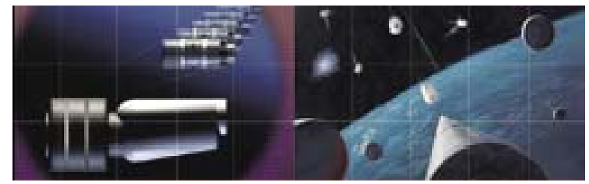
Challenging Initial Requirements

Characteristic	Objective
Density*Isp	3450 Ns/L [2.07 MPa-vac; exp=50]
Vapor toxicity	Does not exceed TLV (No SCBA in handling)
Exhaust carbon content	No soot in exhaust
Melting point	< $2^{O}C$
Detonability	Class 1.3 (Prefer 24 cards maximum in NOL)
Impact sensitivity	> 20 kg-cm minimum (E_{50})
Adiabatic compression	No explosive decomposition (pressure ratio of 35:1)
Thermal stability	< 2% by wt. decomposition (DOT)
Critical diameter	No propagation in lines of < 1.91 cm diameter

Focus- Replace SOTA Hydrazine with Monopropellants Based on Energy Dense Ionic Liquids

Ionic Liquid-based Monopropellants
System Payoffs





<u>Microsat Benefits</u>

120 kg (95 kg propulsion system)
High delta-v required

AF-M315E exceeds
SOTA monopropellant (45%)
and
bipropellant (8%)
Next generation exceeds
SOTA monopropellant (66%)
and
bipropellant (23%)

- **IL-based monopropellants confer higher system payoff in volume limited systems partly due to high density and reduction in system's inert mass fraction**

Toxicity Assessment of AF-M315E

Toxicity Testing Results

- Time consuming
- Expensive

PROPERTY	AF-M315E	HYDRAZINE
LD50 (rat), mg/kg	550	60
Dermal Irritation (rabbit)	None - Slight	Corrosive
Dermal Sensitization (guinea pig)	Non Sensitizer	-
Genotoxicity (Ames)	3 Negative/2 Positive	Positive

- Low hazard
- Low cost

Toxic Vapor ComponentsTesting

NASA White Sands Test Facility –No chemical species detected in the propellant headspace that are identified as carcinogens or have regulated vapor concentration limits (detection limit 2-3 ppb)

AF-M315E Small-Scale Hazards

Test	AF-M315E	Desired
Hazard Class	1.3C (FHC)	1.3C (FHC)
Unconfined Burn (Open container/wood fire)	Test 1 and 3: No reaction Test 2: slow burn	No explosion
NOL Card Gap (O cards)	Negative (deformed plate)	Negative (deformed plate)
Drop Weight Impact Sensitivity (JANNAF Test Method)	126 Kg-cm (E_{50}) Lot 32 Reference material: N-Propyl Nitrate (21 kg-cm)	>20 (E_{50}) Kg-cm
Sliding Friction (Julius Peters –BAM)	352 N (5 consecutive “no go”)	>300N
Thermal (50 ml beaker @75^{o}C/48 hours)	No reaction Wt. Loss < Wt. Volatiles	No reaction Wt. Loss< Wt. Volatiles
TGA (75^{o}C/48 hours)	0.86 Wt % , Excluding Volatiles	<2.0 Wt%, Excluding Volatiles
Electrostatic Discharge	>1J	>1J

Direct Spill- Pan Fire Test

Purpose

Simulate an AF-M315E spill into a JP-8 fuel fire

Results

Test conducted on small-scale (15ml added to 1 gallon JP-8) failed to ignite propellant

At larger scale (1 liter added to 4 gallons of JP-8), denser propellant also falls to bottom of the pan and is ignited when JP-8 is nearly completely consumed

Once ignited (6 min. into test) the propellant exhibited a sporadic luminescent mild burn

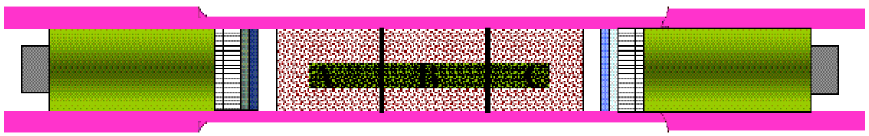
AF-M315E is difficult to ignite at ambient pressure – only catalytic initiation is reliable

JP-8 Fire Prior to Propellant Addition

Ignition of Propellant Near End of Test

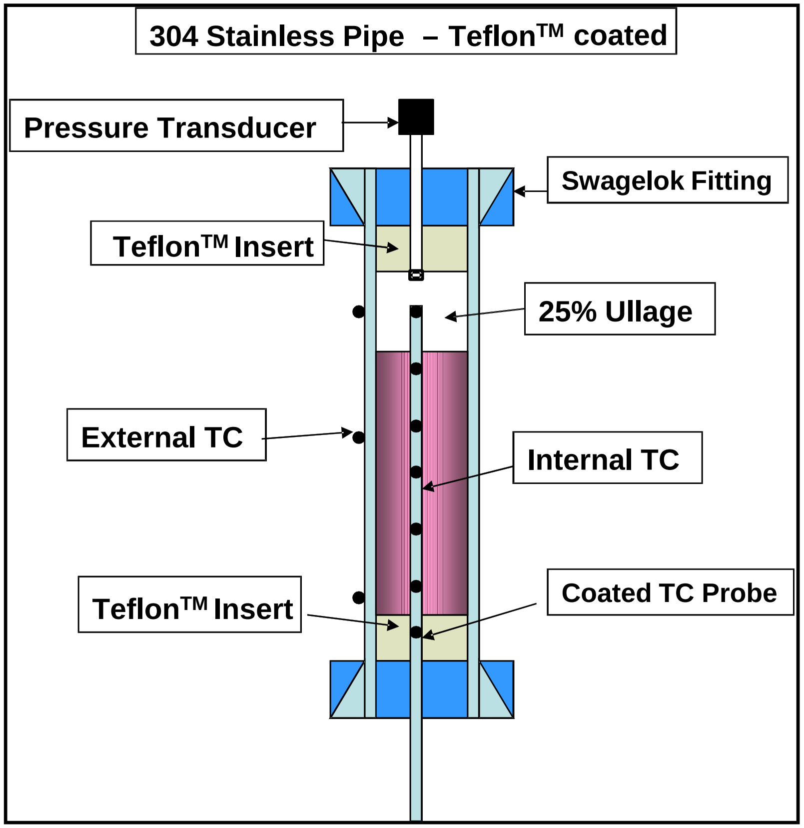
Confined Slow Cook-Off Test Design

Adapted the Standard China Lake 2.54" Cook-Off Pipe in Conjunction with Alice Atwood @ NAWC



- Easier to adapt for liquid testing than the Small Scale Cook-Off Bomb (sealing is an issue)
- Desire internal thermocouples to determine critical temperature of AF-M315E
- Desire a pressure tap to determine rupture pressure
- Desire a burst pressure of ~34.5 MPa similar to a notional propellant tank
- Desire ullage and vertical orientation
- Scalable design (L/D = 3) to full-scale (17.8 cm and 34.3 cm diameter)
- Tested using direct heating

Modified Slow Cook-Off Pipe



Sub-Scale Slow Cook-Off Tests

Joint US Air Force/Navy Design

Test Conditions

- Ramp at 10 deg C/min to 60 ^{o}C
- Soak for three hours
- Ramp at 0.05 ^{o}C/min to cook-off

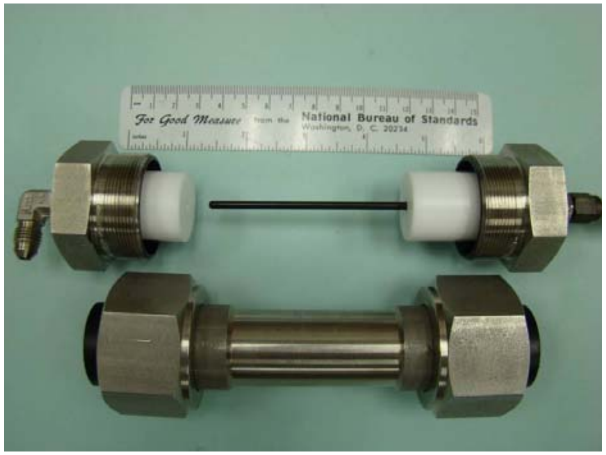
Results

Two tests performed, giving mild case bursts at 48.3 x 10^5 – 55.2 x 10^5 MPa with few fragments

Critical temperature at 2.54 cm diameter was determined to be approximately 140^{o}C

Highest temperatures recorded were in the liquid phase near the liquid/gas interface– probable location of event initiation

Pre-Test 2.54 cm Cook-Off Pipe Assembly



Post Test Cook-Off Hardware

Full-Scale Slow Cook-off Test

Test Conditions
- Soak at ambient temperature.
- Ramp at 0.05 deg C/min to cook-off

17.8 cm Test Results

- No detonation, but strong case burst in center- large fragments recovered; both case ends intact

- Thermocouple data showed,
  - Thermal runaway at ≈ 140°C ; similar to small-scale tests
  - Failure temperature ≈146°C

- The highest temperatures were near the propellant surface

17.8 cm OD Steel Vessel

Top End of Steel Pipe – Post Test

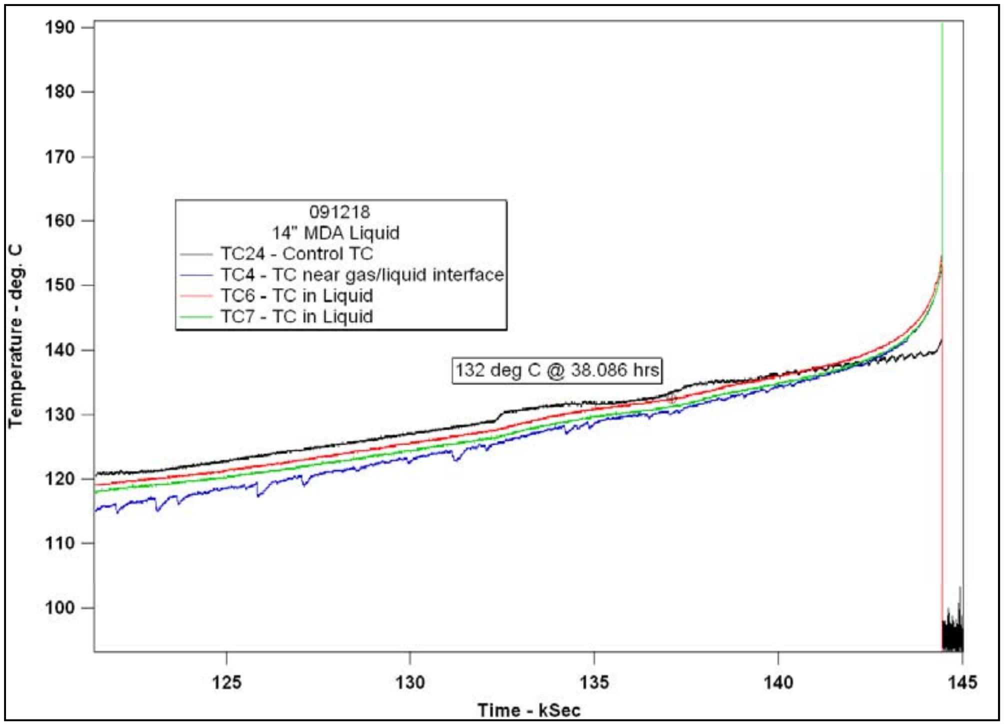
Full-Scale Slow Cook-off Testing

34.3 cm Test

Self-heating started at approximately 132°C – much better than model prediction

Highest temperature near the propellant liquid/gas interface

Failure occurred at approximately 140°C



34.3 cm OD Steel Vessel

Reaction was a detonation

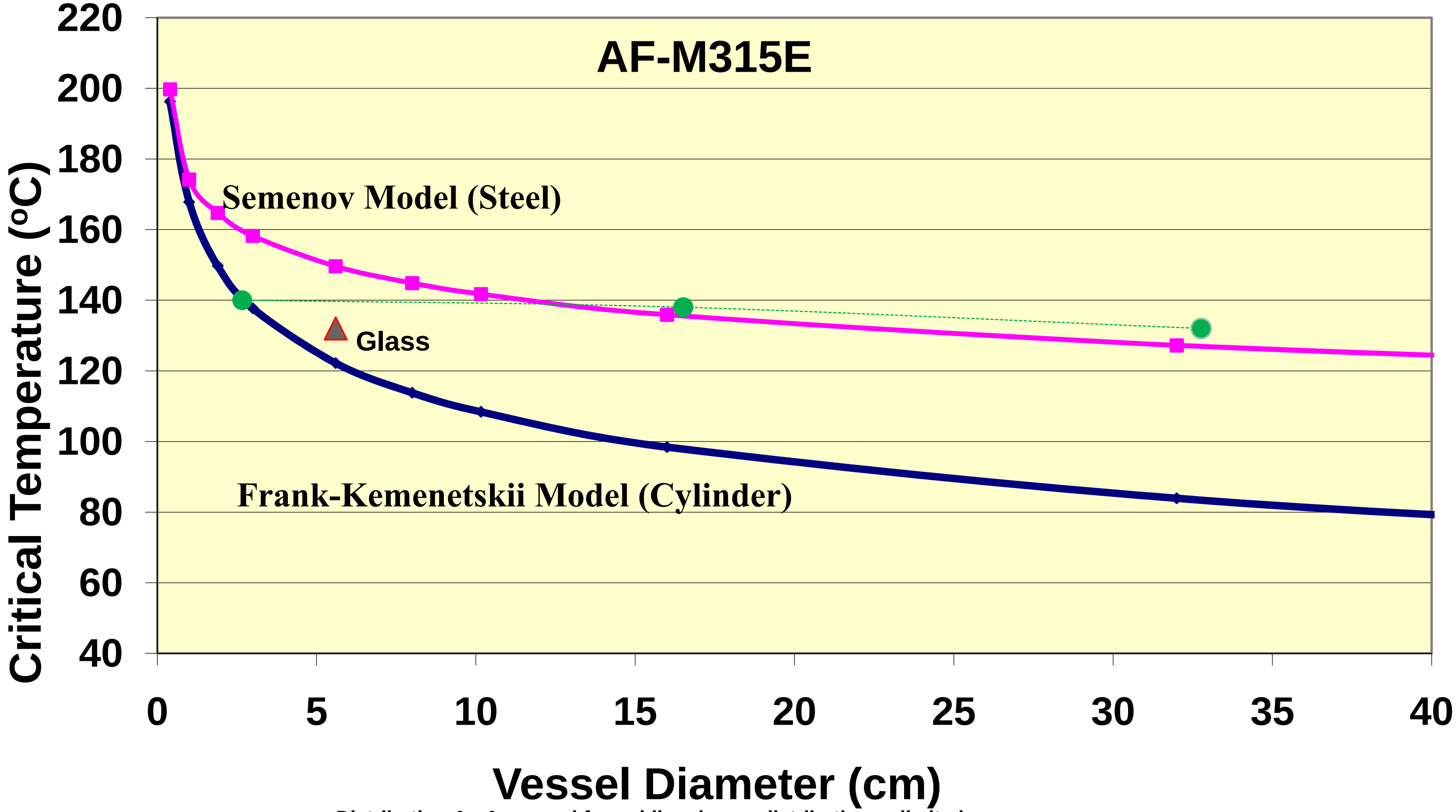
Bikini gauges indicate >103 kPa @ 50ft

Fragments thrown > 185 m

Punched hole in end cap

Critical Temperature Models for AF-M315E

Critical Temperature Models Appear Conservative for Larger Diameters
- Convection takes place in liquids
- Models are heavy functions of Ea which is not predicted well by traditional small unconfined tests



Final Hazard Classification Testing

<u>Test data included</u>: Small-Scale Hazard Data, Single package, External Fire and Super Large Scale Gap Test (SLSGT)

<u>Single packaging tests</u>

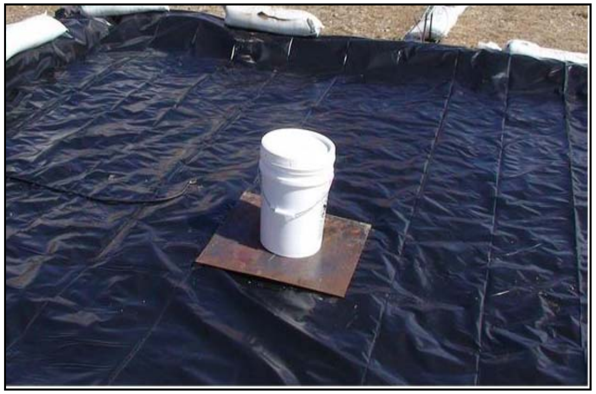
Two packaging configurations identified exhibiting no reaction in single package tests performed in triplicate with a C-4 Donor

- **18.9 liter composite pail containing 25 kg of propellant in a 75.6 liter drum over-pack**

- **3.8 liter poly container (4.54 kg) in a 18.9 liter plastic pail over pack**

<u>Single Package Test</u>

Overpacked 3.8L Container



Post Test

Single Package Testing

Overpacked 18.9 Liter Container

Overpacked 3.8 Liter Container

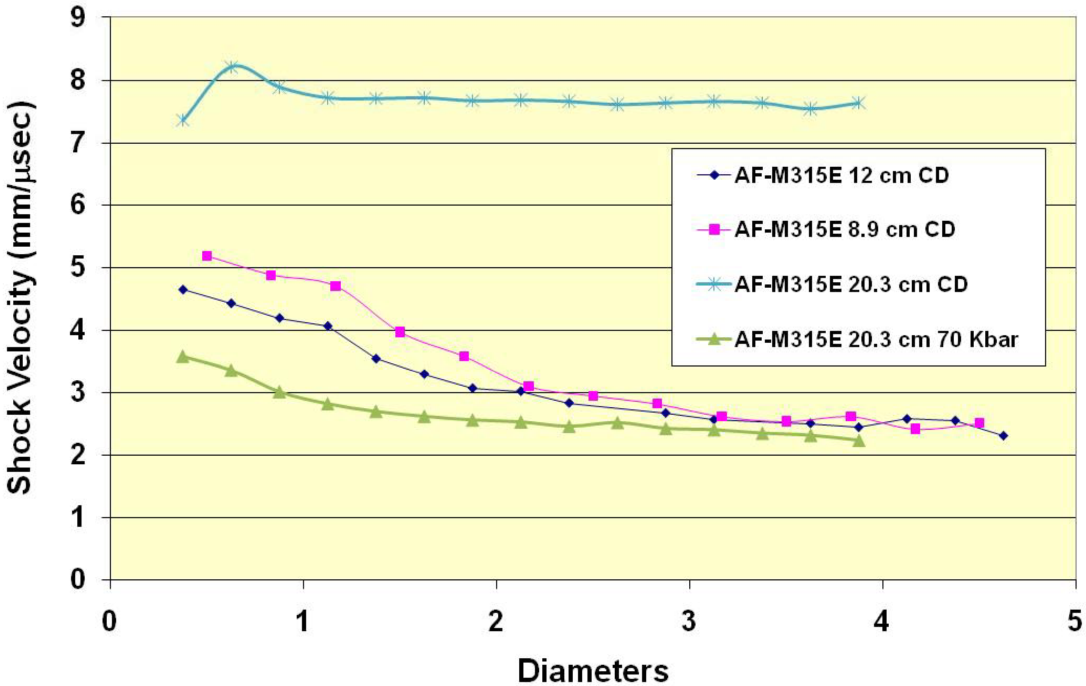
Post Test

Post Test

Super Large Scale Gap Test

Critical Diameter is between 10.16 and 17.78 cm ID

- **Shock decayed to sonic velocity at 70 kbars shock input (1.27 cm Steel Confinement)**
- **Witness plate deformed (no detonation)**
- **Helps differentiate Class 1.1 and 1.3 for propellants**



External Fire Test

Type V – Burning Reaction Desired

SEVERE - (Reaction Response) - MILD

- ✓ MS propellants react violently to shock and impact stimuli

Type I - Detonation Reaction

Supersonic shock wave through energetic material with capability for large ground craters; fragment and blast overpressure damage to structures

Type II – Partial Detonation

Damage depends on the portion of the energetic material that detonates

Type III – Explosion Reaction

Pressure bursts of confined energetic material due to rapid burning; air shock and high velocity fragments can damage nearby structures

Type IV – Deflagration Reaction

Low pressure rupture of confining structure or expulsion of closures; no significant fragmentation, energetic material may be thrown about with heat and smoke damage to surrounding; propulsion of munition might occur

Type V – Burning Reaction

Ignites and burns non-propulsively; no fatal fragments beyond 50 feet

- ✓ MS propellants typically react less violently to thermal stimuli
- ✓ RS propellants react violently to thermal stimuli

Pre-Test Configuration

External Fire Test

Results

- Propellant pails popped their lids and then individually burned mildly 6-8 minutes into the test
- All propellant and inner poly bottles were consumed
- No fragments thrown
- Thermocouples measured the flame temperature up to 776 ^{o}C

Type V – Burning Reaction!

Post Test

Sequence of Events

TIME	EVENT	TIME	EVENT
1:11	POP	5:54	TEST ITEM BURNING
1:27	POP	6:01	TEST ITEM BURNING
1:38	POP	6:22	TEST ITEM BURNING
1:43	POP	7:04	TEST ITEM BURNING
2:00	POP	7:13	TEST ITEM BURNING
2:02	POP	8:07	TEST ITEM BURNING

Substance Final Hazard Classification

US Dept. of Transportation Granted a HD 1.3C Designation For Two Packaging Configurations of AF-M315E

Over-packed 3.8L Container

Packaged AF-M315E Received Final Hazard Classification of 1.3C in August 2010

<u>U.N. PROPER SHIPPING NAME AND NUMBER:</u>
Propellant, liquid, UN0495

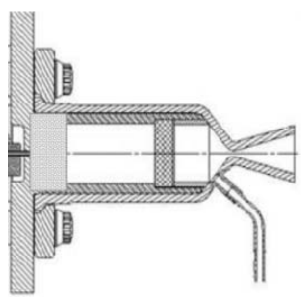
- **18.9L composite pail containing 25 kg of propellant in a 75.6L drum over-pack (EX2010060551)**

- **3.8L poly container (4.54 kg) in a 18.9L plastic pail over-pack (EX2010060549)**

Over-packed 3.8L Container

Spacecraft Chemical Propulsion Demonstration

- **Technology development oriented**
- **Employing <u>advanced catalyst ignition</u>**



SOTA	**N_2H_4**
Propellant	**AF-M315E**
System Goal	**3450 Ns/L**
Demo Objectives	**18 N,** ***30 minute cumulative life***
Challenges	**Catalytic reactivity, high temp & oxidation resistant components (catalyst substrate, bedplate, throat)**

Liquid Engine Alternative Propulsion Development Program (LEAP-DP)

Technology Development

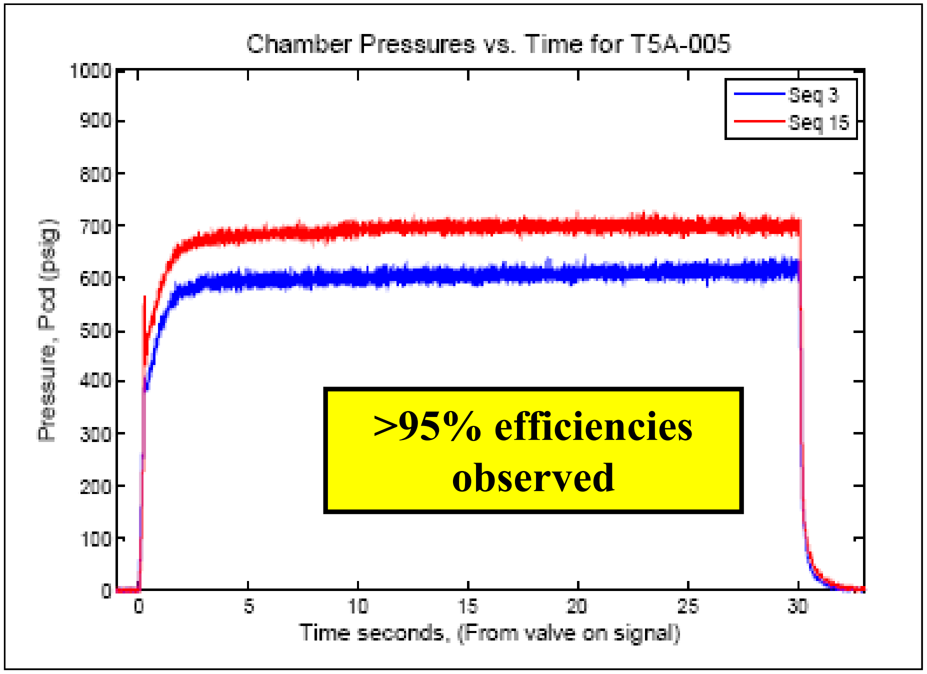
Demonstrate a survivable thruster to meet spacecraft monopropellant goal:
3450 Ns/L [2.07 MPa-vac; exp=50]

- **AFRL sponsored program performed by Gencorp Aerojet , Redmond WA, USA**

Achievements

- **High temperature catalysts and chamber materials capable of withstanding combustion temperature**
- **Good ignition response times**
- **Stable combustion - good chamber pressure roughness**

20 N Brassboard Thruster Pulses



Future work to concentrate on conversion from heavy weight to flight weight hardware

Propellant Performance Characteristics

	LMP-103S	AF-M315E	Hydrazine
Flame Temperature	1600ºC	1900ºC	600ºC
Isp	252 (theor) 235 sec (delivered)*	266 (theor) ~250 sec (delivered)	220-224 sec (1N thrusters)
Density (g/cc)	1.24*	1.465	1.01
Density Isp Increase over N_2H_4	30%*	50%	-
Preheat Temperature	300°C nominal	370°C nominal	315ºC Capable of cold starts (5ºC)
Minimum Operational Temperature	10 – 50 ºC	< 0 ºC System dependent – Propellant becomes viscous, but no precipitation or phase change occurs.	5 - 50 ºC
Minimum Storage Temperature	-7 ºC	Very low (<22ºC) Forms a glass – no crystallization occurs	1ºC (Freezing Point) Reheated for re-use

*Anflo, K. and Mollerberg, R., "Flight Demonstration of New Thruster and Green Propellant Technology on the PRISMA Satellite" ACTA Astronautica, Vol. 65, Nov.-Dec. 2009

Compatibility and Handling

Propellant	LMP-103S	AF-M315E
Thruster Materials Compatibility	High combustion temperature and oxidative environment - high temperature, corrosion resistant refractory metal (Ir and Re) chamber materials needed.	High combustion temperature and oxidative environment - high temperature, corrosion resistant refractory metal (Ir and Re) chamber materials needed.
System Materials Compatibility	Compatible with most COTS materials currently used for N_2H_4 systems. Propellant is basic – compatible with many metals.	Limited material compatibility driven primarily by HAN content and acidity
Handling & Safety	Significantly reduced toxicity removes the need for SCAPE suits	Low toxicity and vapor pressure allow handling with only basic PPE Propellant will not crystallize if concentrated

Status

- Broad range of safety and hazard characterization completed on USAF advanced monopropellant AF-M315E
- AF-M315E has demonstrated significantly reduced toxicity compared to spacecraft monopropellant hydrazine with much higher performance
    - Promises lower testing/operations costs, improved operational responsiveness
    - Leading to next generation systems with increased spacecraft payload, range, and lifetime
- The FHC test data package accepted by DOT for a packaging specific hazard classification of 1.3C for AF-M315E

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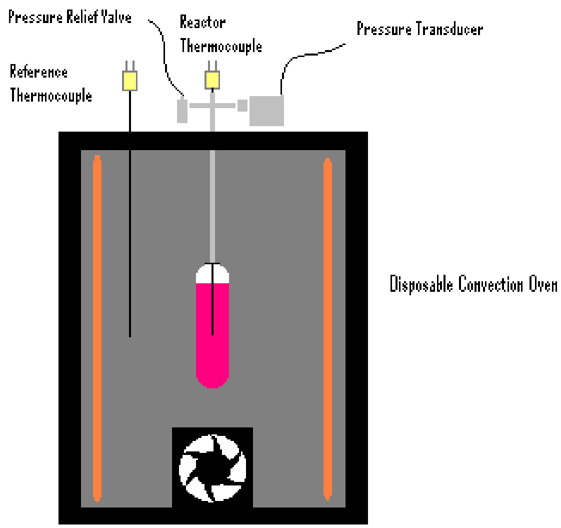
Back-Up Slides

Confined Slow Cook-Off Tests

-Background-

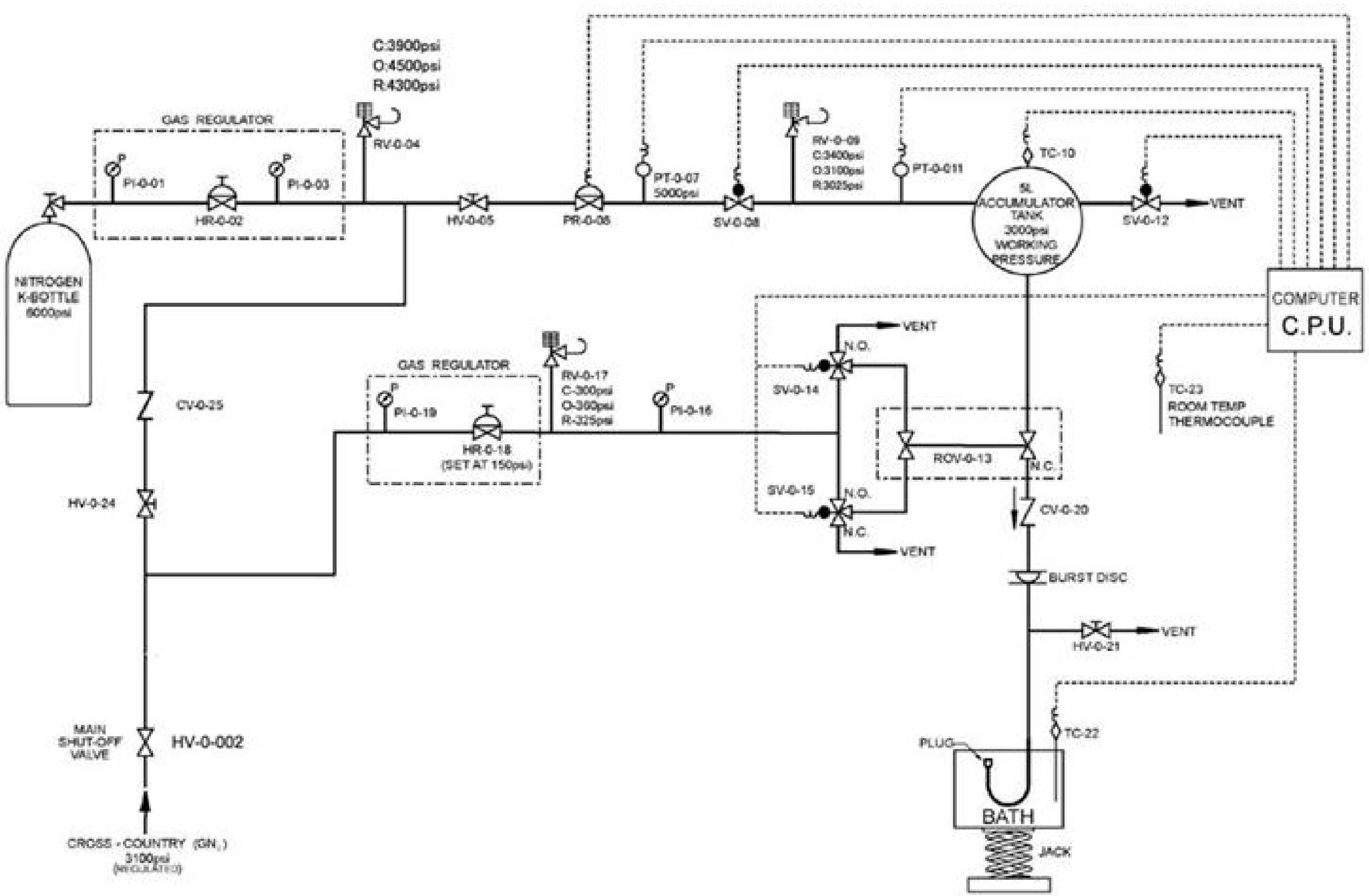
- Wanted Critical Temperature Curve of AF-M315E for Propellant Processing – Similar to 1-Liter Cook-off Test for Melt-Castable Explosives
- New Cook-Off Test Apparatus Designed for Confinement and Propellant Compatibility
  - All Glass High Pressure Vessels
  - Teflon™ or Teflon Coated Couplings and Thermocouples
  - Kraton™ Coated Stainless Steel Tubing
  - Pressure Tap



Confined Cook-Off Test Design

250 ml Confined Cook-Off Oven Assembly

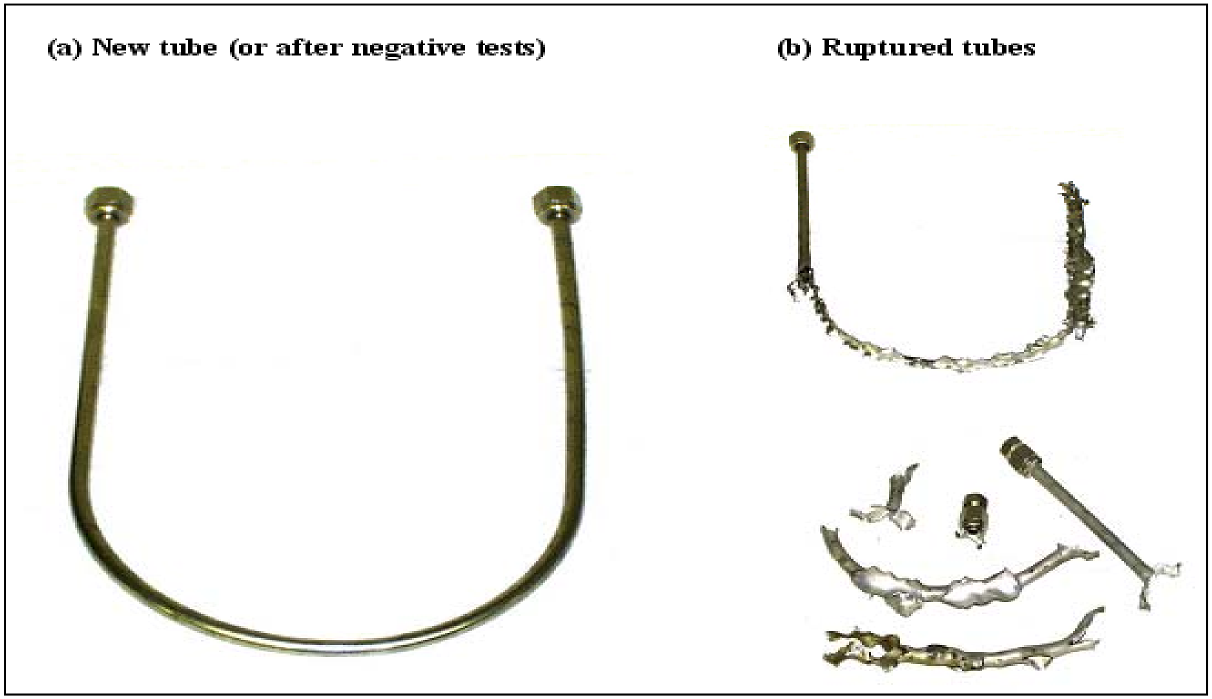
U-Tube Adiabatic Compression



Distribution A: Approved for public release; distribution unlimited

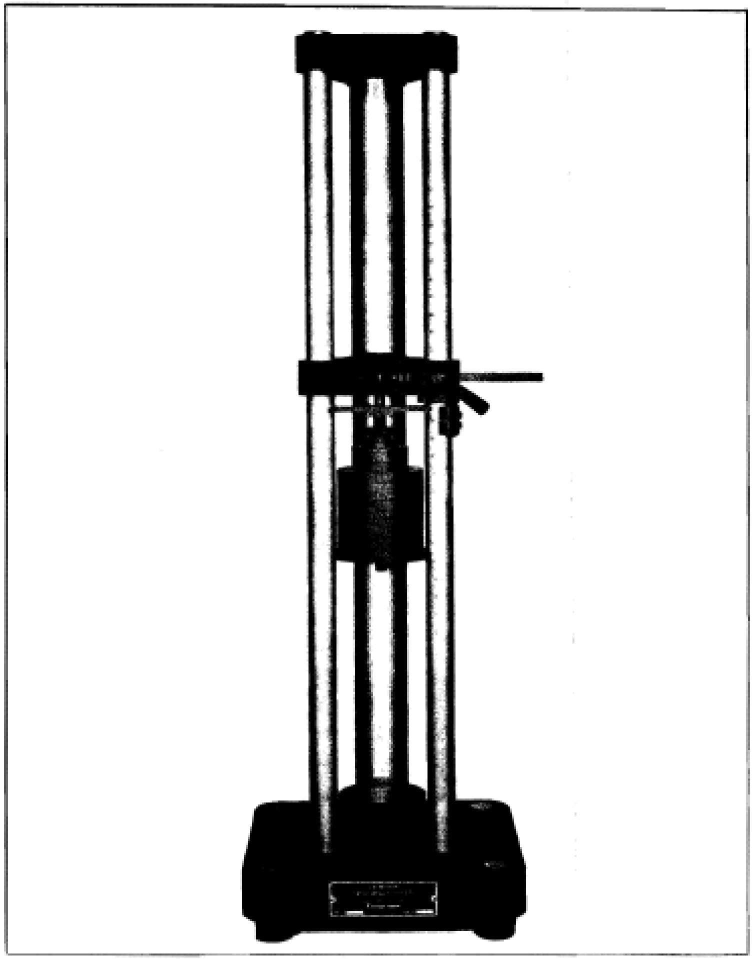
Adiabatic Compression
- continued -

- 3 ml samples are placed in tube
- tube may be heated in a ball bearing bath to desired temperature
- high pressurization rate with N_2 achieved with fast acting valve and a rupture disk
- TIL of 35:1 pressure ratio desired



JANNAF Liquid Impact Test

Olin Mathieson Drop-Weight Impact Tester



Liquid Sample Cell Assembly

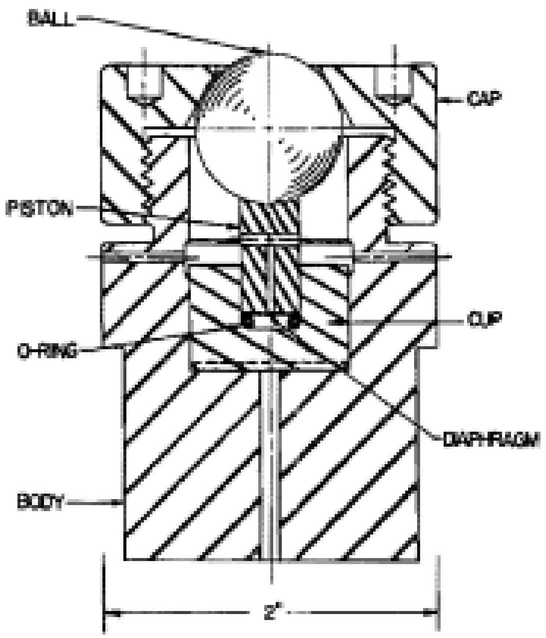


FIG. 1 Sample Cup Assembly

Test is a form of adiabatic compression
- **N-propyl nitrate reference material**
- **Calibrated with water**